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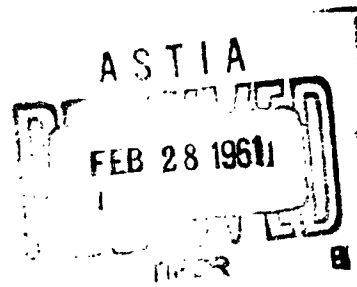
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CATALYTIC EFFECTS IN THE INTERGRANULAR CORROSION

OF HIGH-PURITY ALUMINUM IN HYDROCHLORIC ACID

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## V.  Summary

The major results of quantitative studies of grain boundary and general corrosion in aluminums ranging in copper content from 1 to 600 ppm were:

1.  In 16% HCl where the ratio of the intrinsic boundary-corrosion to general-corrosion rate of an aluminum was estimated as 8, the actual ratio of these rates was made to range up to 50 and down to nearly unity by varying catalytic action through the addition of increasing amounts of cupric ion to the acid.

2.  Boundary corrosion was more rapid with increasing copper content; at least as little as 21 ppm Cu yields a substantial effect and one greater than that of any other residual element.  This behavior was explained as the result of an autocatalytic acceleration produced by the copper introduced by corrosion in a manner similar to that which has been identified for general corrosion.

3.  The view obtained of corrosion in this system is that boundary and general corrosion are related phenomena and change in the same direction but to different extents with changes in copper content or acid composition so that the selectiveness of attack and the geometry of the intergranular crevice can vary widely.  Highly selective attack occurs with conditions under which there is a preferential catalysis of the boundary reaction.

## VI.  Acknowledgements

# CATALYTIC EFFECTS IN THE
## INTERGRANULAR CORROSION OF HIGH-PURITY ALUMINUM IN HYDROCHLORIC ACID

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## I.   Introduction

High-purity aluminum in hydrochloric acid exhibits striking intergranular corrosion and other structure-dependent corrosion phenomena of fundamental interest.  The behavior is highly sensitive to the metallurgical and chemical conditions, the significance of many of which has not been established.  The features of the inter-granular-corrosion phenomenon, first described by Rohrman,[1] are sum-marized in the remainder of this paragraph.  Strong attack normally occurs only at high-angle grain boundaries.[2]  Usually 15-25% HCl is used to obtain a high rate, but this has also been obtained with weaker (7-15%) acid either by adding cupric or ferric ion to the acid[3,4,5] or by passing an anodic current ($\sim 0.1$ ma/cm$^2$).[2,3,5,6]  The two latter corrosion conditions produce strong attack of low-angle boundaries after certain heat treatments.[2,3,4,5,7]  The susceptibility of high-angle boundaries is influenced by the grain-boundary segre-gation of iron atoms; this increases the slow (microns per month) attack in 10% HCl[8] but diminishes the rapid (millimeters per month) attack in 20% HCl[4] (the present and most previous investigations deal with rapid attack).  That segregation of elements other than iron affects intergranular corrosion has not been demonstrated although analysis of data for iron alloys indicated that at least one other

element must be considered.[9] Intergranular attack occurs over a wide range of purity although it begins to become obscured above several hundred parts per million (ppm) total impurities by the severe general corrosion which accompanies the higher iron contents and which is associated with the presence of a second phase or an inhomogeneous distribution of the dissolved iron[4,6,10] The variation of inter-granular-corrosion rate with heat treatment[1,3,4,5,6,8,9,10] can be explained in some cases in terms of the distribution of the iron impurity but is not in general adequately understood.

Although the present investigation began as a study of the effect on boundary-corrosion susceptibility of impurities and solute additions, it proved necessary for it to become primarily a study of the autocatalytic effect of one solute, copper, because of evidence that this effect was significant even for small amounts of copper present as an impurity ($\sim 20$ ppm). The catalytic action occurs as corrosion furnishes ions which cement on the specimen as elemental copper thus providing cathodes of lower hydrogen overvoltage; this effect had been identified previously only in general corrosion and only at higher copper levels ($\gtrsim 1000$ ppm).[11,12,13] The question of boundary corrosion susceptibility did not figure prominently in the present work since the catalytic effect of copper on the corrosion rate (once it had been introduced into the acid) appeared large enough to obscure any influence it had exerted (while in solid solution) on susceptibility. The present work attempted to make the study of

intergranular corrosion more quantitative than it had been and placed
emphasis on the comparison of intergranular and general corrosion,
both because the two are believed to be related phenomena and because
detailed information on general corrosion can be obtained readily and
can provide clues to intergranular-corrosion mechanisms. Part of the
work dealing with the autocatalytic acceleration of general corrosion
by copper has been reported separately[14] and is reviewed in Section
III.C.1..

### A. Material

The aluminums procured (Table I) represented three low copper (1-3 ppm) lots, two of "normal" copper content (21-22 ppm), and two dilute copper alloys based on one of the latter (several additional alloys are shown in Ta ble III). Iron was held as low and as constant as possible. The only elements found in unsuspectedly large amounts were several in zone-refined aluminum $\cancel{A}$ (the startling figure for Mg is not in doubt). The upper limit for elements not listed in Table I can be set at 5 ppm (somewhat lower in a few cases); the present data, like the others in the literature, do not exclude the possibility that a number of these elements of lower analytical sensitivity are present at the 1 ppm level.

Test acid was made up from two lots of selected 37½% HCl CP reagent containing 0.1 ppm heavy metals, 0.05-0.06 ppm Fe and $<0.008$ ppm As and from water distilled from 1 megohm-cm demineralized water. Acid strength was adjusted to within 0.05% HCl of the stated value with the aid of precision hydrometers.

### B. Procedure

The procedure was based on one employed previously.[4] Blanks 10x41 mm sheared from 1.65 mm cold-rolled sheet, with edges finished by filing, were annealed in air at 645°C for 24 hours in alundum boats and water quenched. The total time of quench was measured as about 0.15 sec. The choice of heat treatment was governed by the following considerations: (1) it produced an average grain size of 3 mm or

more so that many grains had diameters at least three times the sheet
thickness and boundaries running nearly normal to the surface (2) it
was conducive to the attainment and retention of a homogeneous solid
solution within the grains  (3) it minimized grain-boundary segregation
and resulting differences in corrosion susceptibility.  Neither (2)
nor (3) is satisfied with a lower cooling rate.  The by-products of
quenching were not objectionable - there was no evidence any quenching
strain was significant for corrosion and any effect produced by the
dislocation loops formed by vacancy condensation[15] would have been
the same for all the aluminums studied (the as-quenched structure
changes at much higher solute concentrations[16]).  The annealing time
was quite sufficient; specimens of A, B and C annealed one month
contained fewer small grains and somewhat straighter boundaries but
showed no significant difference in corrosion behavior.

The specimens were etched 6 min. in $37\frac{1}{2}$% HCl (0,01-0.02% weight
loss) to hasten the removal of the oxide film during the test for
which they were placed on their long edge (held erect by a glass sup-
port) in 200 ml of test acid in a loosely covered 400 ml beaker
maintained at 24.0 $\pm$ 0.3°C.  The rate of hydrogen evolution (this is
equivalent to the rate of weight loss) and the surface appearance were
viewed frequently at magnifications up to 25X; at appropriate times
the specimen was removed with a forceps equipped with long Teflon
tips and held momentarily against a strong beam of light in a darkened
room for determination of the time when corrosion had progressed

through the specimen at a given number of boundaries (see Fig. 2b and c). The test was normally terminated when about ten boundaries had corroded through, shortly before the specimen began to separate into grains.

## III. Results and Discussion

A. General Quantitative and Morphological Considerations

The behavior of Aluminum A served as the point of departure and is illustrated in Figs. 1 and 2.

1. Acid Stability - This is important because of the sensitivity of the corrosion rates to acid concentration (Fig. 1), especially in the studies of corrosion versus time discussed later. To use the 16% HCl data for illustration, the acid strength tended to decrease (by 0.4% HCl at the end of the test) because of the consumption of hydrogen ion by corrosion and tended to rise because of the preferential evaporation of water vapor ($p_{HCl}$ is only 0.06 mm while $p_{H_2O}$ is 16 mm as compared with 6 mm for the laboratory air at 40% R.H.). The latter effect was shown in a 16% HCl blank, which rose at rates from 0.4% to 1.4% HCl per month, and, as checked by the observed decrease in acid volume, was responsible for the scatter in intergranular-corrosion rates of specimens exposed to 16% HCl at different periods. Test conditions were normally designed to avoid excessive exposures and high weight losses were encountered only in strong acids so that, with a few exceptions, the net change in acid concentration would not have exceeded a few percent of its original value.

2. Intergranular Corrosion Rate - 20 to 30 high-angle boundaries

in a specimen were readily corroded through (the ones more slowly
attacked presumably represented special orientation relationships and
special orientations of the boundary plane). Since the times required
differed by less than a factor of two (note the high slopes in Fig. 1)
and since some of the spread was attributable to variations in path
length with boundary inclination, the time for the first boundary to
corrode through (penetration time) could be used as a fair character-
ization of the lot. This parameter was insensitive to normal grain-
size variations, which affected the slopes rather than the intercepts
shown in Fig. 1. It may be noted that the susceptibility changes
produced by strong iron-atom segregation are reflected in both inter-
cept and slope.[9]

3. General Corrosion - The thinning of the specimen was in every
instance rather uniform although there were variations in morphology
and large variations in the amount of general corrosion at the end of
the test, which represented a fixed amount of boundary corrosion.
Fig. 2a shows only macroscopically uniform thinning (microscopically
a 10 micron cubic pit and step pattern). In Fig. 2b, a localized-
corrosion trench pattern (of the same crystallographic nature) has been
been superimposed; this was produced by the autocatalytic reaction
associated with the copper in the aluminum. In Fig. 2d, the localized-
corrosion reaction had developed over the whole surface, which was
rougher than that of 2a. In these cases of deep intergranular attack
the mouth of the intergranular crevice was about twice the depth of

corrosion of the surface; differences in crevice geometry were considered merely reflections of the difference in the extent of the general corrosion of the walls of an inherently narrow ($\sim 10$ A°) grain-boundary corrosion zone. In the extreme case where intergranular and general attack proceeded at substantially the same rate (Fig. 2e), there was only a shallow intergranular groove.

The variation in depth of attack from one grain to another was not normally noticeable because of the coarsening texture, the sheet surface lying in the neighborhood of (100) in most grains. In grains oriented otherwise the depth of attack tended to be greater, as would be predicted from Bussy's analysis[6] of the corrosion rate in any direction as the resultant of the rates along $\langle 100 \rangle$.

The relatively uniform thinning permitted micrometer measurements on a number of specimens; a plastic sheet was interposed to take up some of the fine roughness. It was estimated from these measurements that the general corrosion of the specimen surface accounted for 85% or more of the weight loss in any specimen. The weight loss could therefore be used as the measure of general corrosion; its relative independence of the progress of intergranular attack was associated with the coarse grain size and the relatively small total volume of the intergranular crevices.

4. Significance of Initial Surface Condition - Each test began with a stage of low corrosion rate during which the etching of the metal beneath the oxide film (initiated in patches by the preliminary concentrated acid treatment) spread over the surface until the oxide film was completely detached to be replaced by a film characteristic

of aluminum in the acid environment. This process occupied at most 15% of the test period so that the behavior was detmined substantially by the properties of the aluminum with respect to the test acid. In other investigations, strong initial protection of the surface has been noted with films produced by electropolishing[2,5,6] or by exposure to weak hydrochloric acid.[4]

B. Comparison of Intergranular with General Corrosion in Aluminum A

A direct comparison of intergranular and general corrosion was made by converting penetration time and weight-loss data to average rates of penetration for boundary ($\bar{R}_B$) and surface ($\bar{R}_S$). With increasing acid (Fig. 3) or cupric ion (Fig. 4) concentration (the original composition is the same), the rates rose rapidly at first and then more slowly. The attainment of a limiting rate could be displayed in Fig. 4 and was suggested in the behavior of $\bar{R}_B$ in Fig. 3, but this could not be examined further in Fig. 3 because of the onset of the passivation shown at higher acid concentrations. This passivation was noted in commercial aluminum (under nitrogen atmosphere) by Berg[18] who attributed it to adsorption of non-ionized HCl. That the maxima in $\bar{R}_B$ and $\bar{R}_S$ in Fig. 3 were not due to some extraneous circumstance such as the presence of an unknown stimulating agent in the water used to dilute the acid reagent was shown by the satisfactory checks obtained in two tests for which the reagent strength had been reduced by preferential evaporation of HCl.

Silver ion additions up to 0.8 ppm yielded results close to those shown in Fig. 4.

The corrosion in 16% HCL is under cathodic

control as indicated by the strong catalytic stimulation produced by the cementation of metals of low hydrogen overvoltage. Hydrogen-overvoltage data which can be applied with confidence to the present system are not available; in view of the large potential difference which would exist between the unpolarized anode and cathode reactions, it appears that this overvoltage must be one volt or more at the lower corrosion-current densities of the present work ($10^{-4}$ amp/cm$^2$). The cathodic reaction is stimulated by increasing the abscissa in either Fig. 3 or Fig. 4, which accounts for the broad parallelism (apart from the passivation) between the two (an increment of 0.1 ppm $Cu^{++}$ is equivalent to increasing the acid strength by 1 to 3% HCl). The potent effects of $Cu^{++}$ additions arise from the reduction of the overvoltage to 0.3-0.6 volt, the values for metallic copper in the current-density range for the data in Fig. 4, at those cathodes where copper has cemented. The steepness of the initial rise of the rate curves in Fig. 3 represents contributions from three factors: the activity coefficient is rising so that the activity of the acid increases almost exponentially with percentage HCl, the stirring effect of the hydrogen gas evolved increases as the corrosion rate rises, and the auto catalytic effect of the copper introduced by cor-rosion increases with increasing acid strength.[14] The highest rates shown in Figs. 3 and 4 are not the highest possible, as discussed below.

It is noteworthy that $\bar{R}_S$ and $\bar{R}_B$ responded in a similar manner to changes in acid composition, the maximum in their ratio being the

result of the steeper initial rise and earlier leveling off of $\bar{R}_B$.

Below 16% HCl, it was qualitatively evident that this ratio decreased, and it was measured as 1½ for 1% HCl (the additional intergranular penetration was determined by the focussing method). The high ($\sim$50) values of this ratio near the maxima in Figs. 3 and 4 represent specific chemical conditions. The choice by many investigators of such conditions yielding rapid and selective intergranular attack has tended to produce an incorrect impression of this phenomenon which is viewed more accurately as one where corrosion is faster at the boundaries rather than one where corrosion is practically confined to the boundaries.

C.  Effect of Copper Content

In this part of the work, a more informative technique was available for general corrosion and it was studied separately.

1.  General Corrosion – This had been measured as a function of time by collecting the evolved hydrogen. For 20% HCl (Fig. 5), the four hydrogen-evolution curves previously reported[14] were confirmed and supplemented at a number of points by weight-loss data obtained in beaker tests of the seven aluminums. Fig. 5 shows that the different lots having the same copper content behaved in substantially the same way and that the hydrogen curves provided a satisfactory representation of the behavior at each copper level. The stages of corrosion (and their morphological features) were[14]:  (I) an induction period of low corrosion rate (etching of the surface and stripping of

the oxide film)   (II) a stage of constant rate, the intrinsic cor-
rosion rate of the solid solution, which did not vary significantly
with with copper content (uniform etching attack, Fig. 2a) (III) an
autocatalytically accelerating stage which began abruptly only after
some corrosion had occurred, the inception being earlier and the
acceleration greater the higher the copper content (localized attack
superimposed on the uniform etching, Fig. 2b).  The morphology was
the same for all aluminums except that the autocatalytic reaction
at 600 ppm Cu took place in pits rather than in the trenches shown
in Fig. 2b (see Fig. 8) and that the high localized accelerations at
140 and 600 ppm Cu tended to yield macroscopic roughening of the
surface, in contrast to Fig. 2d.

Increasing copper content led to a reduction in the duration of
Stage I but its principal effect was exerted through the autocataly-
tic reaction so that the large differences between aluminums of dif-
ferent copper content did not become manifest until one of them
reached Stage III.  It was difficult to show this large ultimate
difference in the case of the 21-22 versus the 1-3 ppm Cu aluminums
since the required exposures of 200 hours or more were feasible with
the former only with a few specimens which were unusually coarse
grained, these being the only ones which did not disintegrate inter-
granularly before this time.

An identifiable autocatalytic reaction did not appear in these or
any other tests on the 1-3 ppm Cu specimens nor below 18% HCl with
the 21-22 ppm Cu specimens.  In the absence of this reaction, the
intrinsic scatter of the data was small.

The effects of introducing copper by corrosion were quite different from those obtained by adding cupric ion to the acid. The latter, as with increasing acid strength, yielded higher corrosion rates but the acceleration remained low (it was this fact which permitted the use of average rates). Also, the (average) rates shown in Fig. 4 were at most 0.6 mm/day even with 5.5 mg (25.6 ppm) cupric ion, while the autocatalytically accelerated rate in the 600 ppm $Cu$ aluminum reached much higher values and was measured at the equivalent of 10 mm/day at a point where only 0.05 mg of copper had been introduced by corrosion. The greater potency in the latter case has been explained as the result of the cementation of elemental copper in metallic contact with the aluminum rather than over the surface film.[14] It is because the autocatalytic acceleration is detectable after the introduction of as little copper as 0.1 microgram/$cm^2$ that it can become important at copper contents (at least) as low as 21 ppm.

2. Intergranular Corrosion - Experimental methods like those of the previous section were not readily available for intergranular corrosion and the standard method was used. In Fig. 6, the penetration times of the seven aluminums are shown over a range of acid strengths. For high copper contents, the behavior became awkward in strong acid where the autocatalytic acceleration produced catastrophic general corrosion rates before penetration was complete. This made it impossible to follow the intergranular disintegration as in Fig. 1 and in some cases led to heating of the solution, but it did not prevent determination of an intergranular-penetration time since the puncturing occurred first at a grain boundary (Fig. 7).

For lower copper contents (1-22 ppm), it is to be noted that the penetration times in 16% and 14% HCl tended to appear lower than the correct ones because of the rise in acid strength (Section III A.1) during the long exposures.

To the extent that the penetration times pertain to the general high-angle boundaries present in every specimen, none of the differences in the behavior of the different aluminums was attributable to texture or grain=size differences. Exceptions occurred in Aluminum H (the two isolated triangles in Fig. 6) where many specimens had so few boundaries that it was not fair to assume that some general high-angle boundaries were present. It may be noted that the grain-coarsening tendency varied **inversely with iron content** in these aluminums; this effect is not, with the present iron contents, due to the presence of a second phase[19] and it appears related to the interaction between migrating boundaries and dissolved impurities demonstrated in aluminum at lower temperatures.[20]

The penetration times in Fig. 6 at a given acid strength decreased with increasing copper content, there being no significant difference between different lots at the same copper level. Increasing the copper content was analogous to increasing the acid strength. This was also true for general corrosion; for example, the penetration times and relative amounts of intergranular and general attack with 600 ppm Cu in 1% or 14% HCl roughly duplicated those obtained with 21 ppm .u in 16% or 30.3% HCl.

Of the two ways in which copper content can influence inter-granular corrosion, the catalytic effect is believed from the general corrosion results to be so large as to obscure any susceptibility effect arising from copper-atom segregation in the grain boundaries. Evidence of an intergranular autocatalytic reaction at 600 ppm Cu was sometimes obtainable from the corrosion morphology (Fig. 8) and from the sharply rising rate of intergranular penetration indicated by examination of specimens removed from the acid before penetration was complete. There was normally no way to detect the presence of an intergranular autocatalytic reaction (unlike general corrosion where the morphology changes) and such a reaction may have been present even with the 1-3 ppm Cu aluminums. It is to be noted that Montariol[5] observed slower intergranular and general attack at 0.06 ppm Cu than at 2 or 4 ppm.

3. Intergranular Penetration Versus Time - A susceptibility effect, which is present throughout the test, can be distinguished from an autocatalytic effect, which is initially absent and increases as corrosion progresses, with information on corrosion as a function of time, as was done for general corrosion. For investigating inter-granular corrosion, steps were milled in 26x78 mm blanks to provide six thicknesses. After annealing, each step contained many grains having diameters three or more times the step thickness so that the penetration-time method could be applied to each step. Results are

given in Fig. 9 for Aluminum A in two acids for which general-corrosion
data were available. For general corrosion, the three stages were
distinguishable in 20% HCl but in 16% HCl the slight rise in slope
was too low to be identifiable as the autocatalytic acceleration since
a rise in acid strength may have been responsible for it (this comment
does not apply to the 16% HCl step test where the volume of test acid
was larger, in correspondence with the larger specimen area, and the
acid strength changed very little). Intergranular penetration would
be expected to occur in the same three stages since intergranular and
general corrosion are considered related phenomena in this system
(Section IV.A). The boundary penetration curves obtained were some-
what similar to those for the surface but the resolving power of the
method was too low, because of the experimental scatter and the small
number of steps, for a satisfactory description of the intrinsic and
catalytic stages.

It is to be noted that if the autocatalytic effect is greater for
boundary attack than general attack, this can exaggerate the initial
intrinsic rate difference and yield abnormally high $\bar{R}_B/\bar{R}_S$ values. For
example, if boundary attack starts sooner to experience the same auto-
catalytic acceleration, at any later time it will have suffered a
greater increase in rate than general attack. Some such situation is
thought to be responsible for the high $\bar{R}_B/\bar{R}_S$ values in Aluminum A
(21 ppm Cu) near the maximum in Fig. 3. For 20% HCl, this ratio is
lower by a factor of two for the low copper (1-3 ppm) aluminums con-
sistent with the smaller autocatalytic effects expected. For
Aluminum A in weaker  acid, the acceleration is lower and the average rates

would be closer to the intrinsic ones; thus for the 16% HCl data in Fig. 9a, the ratio of intrinsic boundary to surface rate estimated from the data up to 20 days is 8 and $\bar{R}_B/\bar{R}_S$ computed for the last step is 10. Attempts are under way to refine the method for further study of the questions raised in this section.

## D. Effects of Some Other Elements

Exploratory tests were made on several dilute alloys (single phase as quenched from 645°C) involving elements present in much smaller quantities in high-purity aluminum. Results in 20% HCl are given in Table II. Although the additions were relatively large, in no case is a large effect on intergranular or general corrosion indicated, and it is the incidental variation in copper content (and perhaps in iron content, for the manganese alloy) which seems to have been responsible for many of the differences in the Table. The corrosion morphology was in all cases indistinguishable from that of Lot A. Von Zeerleder and Zurbrügg had previously noted that additions of these quantities of Mg, Si, and Mn (also Zn) produced little or no increase in the rate of general corrosion in 10% HCl for specimens quenched from 500°C[21]. Bussy reported no major modifications in behavior resulting from small (unspecified) additions of Ga and Mn.[6] Previous work on iron additions, which reduce the rate of intergranular attack, showed no large influence on general corrosion other than the one associated with an inhomogeneous distribution of the dissolved iron,[4] the diffusion rate of which is apparently low compared with those of other solutes.

For additional reassurance that, other than copper, no element in the aluminums studied was catalytically sufficiently potent to require investigation, additions were made to the acid of the ions of several relatively low overvoltage or noble metals present or possibly present in the aluminum at the 1 ppm level. The effects found for $Ag^+$ and $Ni^{++}$ (Table III) did not exceed that of $Cu^{++}$ so that there was no reason to suspect that the Ag and Ni in these aluminums would have had an effect greater than that of 1 ppm Cu.

The result that $Pb^{++}$ had no effect at 0.8 ppm (note that this represents a substantial quantity of lead, equivalent to 70 atom layers over the nominal specimen area) but was effective at 100 ppm can be explained if the hydrogen overvoltages of high-purity aluminum and lead are not very different so that the effect lies only in the increased cathode area provided when considerable lead cements in the form of loose or spongy masses; such masses were observed clinging to the specimen at 100 ppm. That intergranular corrosion was enhanced much more than general corrosion is in line with the result for $Ni^{++}$ at 0.8 ppm and for $Cu^{++}$ and $Ag^+$ in smaller amounts and thus appears to be a general characteristic for additions which do not produce saturation of $\bar{R}_B$.

The first two sets of figures in Table III for rate of weight loss illustrate the general observation that the experimental scatter was large only when catalytic action was strong. The scatter of the 0.8 ppm $Cu^{++}$ data was the largest recorded.

The heavy metal ion content of the acid reagent would appear at
0.04 ppm in the 16% test acid.  This impurity is reported by the manu-
facturer to be mainly lead, which the present data indicate to be
without effect at this level, together with small amounts of manganese
and of copper, which has a substantial effect at 0.05 ppm (Fig. 4), so
that the influence of the reagent impurity is regarded as having been
quite small but not necessarily negligible.  Metallic impurities in
the water were considered negligible since the results of two corrosion
tests involving acid made up with water which had been only deminer-
alized were not different from those for which the water had been
purified further by distillation.

### IV.  Additional Discussion

A.  Relations Between Intergranular and General Corrosion

There are strong reasons for believing that intergranular and
general corrosion are closely related here.  The grain boundary in a
single-phase alloy is only a strip of lattice defect which extends for
a few atom layers and, although it may have a higher solute content
than the grain body, there is nothing in its structure pointing to
a unique corrosion mechanism distinct from the one involved in general
corrosion, especially since the grain body also contains lattice
defects (subboundaries and distributed dislocations) which fit the
same description and which may be involved in general corrosion.  An

additional point is that the grain-boundary corrosion cell has a grain-body cathode in the walls of the intergranular crevice. Thus the view advanced here is that the grain boundary and grain-body local cells differ only in that the former have a more active anode. The experimental results (Section III. B) are consistent with this view.

The result, implicit in this view, that the general-corrosion rate was always a significant fraction of the boundary rate is of importance in regard to the broadening of the original grain-boundary crevice; this is a necessary condition for the deep and rapid intergranular penetration observed since a "pure" grain-boundary attack producing a crevice $10°A$ wide would soon be stifled. In the present system, depolarization of the boundary corrosion reaction is further aided by the stirring effect of the hydrogen produced within the intergranular crevice by the general corrosion of its walls. It may be noted that although general corrosion is an important factor in grain-boundary attack the reverse would not be anticipated in a single-phase specimen since so little current is required for the corrosion of the narrow boundary zone.

The system $Cu_3Au$ in ferric chloride is another case where a single-phase alloy suffers deep intergranular attack accompanied by significant general attack; an autocatalytic effect, present because corrosion yields a gold sponge cathodic to the alloy, is a major factor in extending the depth of attack.[22]

## B. Effect of Solute Segregation on Intergranular-Corrosion Susceptibility

No comment can be offered on the basis of the present results regarding any possible susceptibility effect associated with copper content. For the different lots at the same copper level in Fig. 6, there was no indication that variations in other residual elements had substantial effects. The solute content at which an observable susceptibility effect appears is known in the case of iron, the grain-boundary segregation of which reduces the susceptibility in 20% HCl as shown in a previous study using similar procedures.[4,9] For specimens quenched from 647° C, the intergranular-penetration rates of lots containing 4 and 40 ppm Fe (atom fractions $2 \times 10^{-6}$ and $2 \times 10^{-5}$) differed by only about 20% (a higher iron content or lower annealing temperature produced more substantial effects). The influence of iron-atom segregation would therefore have been small for the aluminums in Fig. 6 where iron contents did not exceed 10 ppm. All the impurities in these aluminums, with the exception of magnesium in H and silicon in A, are in this low range (atom fractions not in excess of $10^{-5}$). None of the other studies of this intergranular-corrosion phenomenon has indicated that impurities at the 10 ppm level play a dominant part or has failed to observe intergranular attack. Thus none of the evidence suggests that solute-atom segregation is required for intergranular-corrosion susceptibility (the case of iron is just the reverse). This possibility can not strictly be ruled out since grain-boundary segregation of one or more elements at the saturation level

in the purest material studied would also account for the observed insensitivity to composition variations or solute additions.

## C.  Catalytic Effects from Cation Additions

The saturation of $\bar{R}_B$ and $\bar{R}_S$ in Fig. 4 is identified with the condition where all the grain boundary and body local cells have copper cathodes, the corrosion rate being unaffected by increases in the thicknesses of the cemented copper patches.  The noteworthy feature is the large amounts of $Cu^{++}$ required for saturation.  $\bar{R}_B$ and $\bar{R}_S$ began to level off at 0.2 and 0.8 ppm and became almost level at 0.8 and 3.2 ppm.  If the cementation had occurred in a uniform manner, 0.01 ppm $Cu^{++}$ would have been sufficient to form a copper monolayer based on the nominal area.  The unknown geometrical factors will not be great enough to account for the difference between this figure and the ones observed.  The implication is that the patches of cemented copper differ in thickness from one cathode area to another and are absent from some below saturation (the distribution changes with time, as the copper patches become undercut by corrosion and reoxidized to $Cu^{++}$, so that the observed attack is macroscopically uniform).  That $\bar{R}_B$ saturated earlier than $\bar{R}_S$ is taken to indicate that cementation occurs preferentially at the cathodes serving the grain-boundary reaction.  This is consistent with the larger initial effect on the boundary rate produced by cation additions.

That $\bar{R}_B/\bar{R}_S$ could be varied in Fig. 4 up to 50 (or down to near unity) by manipulation of catalytic conditions while the suscepti- bility ratio remained constant at 8 (Fig. 9a) is significant in con- nection with the subgrain-boundary corrosion phenomenon noted after certain heat treatments in specimens with a coarse substructure.[3,4] The subboundary corrosion susceptibility at its maximum (explained as the result of the condensation of lattice vacancies on the disloca- tions composing  the subboundaries[7]) is only slightly greater than the general-corrosion susceptibility and the phenomenon can be observed only with specific acid compositions, such as 7% HCl containing 0.5-1.0 ppm $Cu^{++}$. The present data suggest as the significance of this acid composition that it is the one which produces the subgrain- boundary equivalent of the high narrow $\bar{R}_B/\bar{R}_S$ peak in Fig. 4 so that the difference between subboundary and surface corrosion rates then becomes substantial.  It would appear that an analogous situation exists when cations, such as those of gold or copper, are added to enhance the sensitivity of mixed acid etchants used in the examination of substructures in aluminum.[23]

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## Table I

### Elements Detected in Spectrographic Analyses of Seven Aluminums* - Parts Per Million

| Lot | Cu | Fe | Si | Mg | Na | Cd | Zn | Ag | Mn | Supplier |
|-----|----|----|----|----|----|----|----|----|----|----------|
| E | 1 | 1 | $<3^+$ | 100 | 2 | <1 | 5 | <1 | $<1^+$ | I |
| K | 1 | 4 | 4 | 3 | 1 | <1 | $<5^+$ | <1 | $<1^+$ | I |
| M | 3 | 5 | 10 | 10 | 1 | 2 | $<5^+$ | <1 | <1 | II |
| P | 22 | 4 | 6 | 4 | 1 | <1 | $<5^+$ | <1 | <1 | II |
| A | 21 | 10 | 30 | 5 | 2 | 3 | $<5^+$ | <1 | <1 | II |
| B** | 140 | 10 | | | | | | | | II |
| C** | 600 | 10 | | | | | | | | II |

*Supplier's data supplemented and checked by Johnson, Matthey and Co., Ltd. and another analytical laboratory    1 ppm = 0.0001 w/o.

**Cu added to A          + Not detected

Supplier I - Aluminium - Industrie-Aktien-Gesellschaft, II - Aluminum Company of America.

## Table II

### Corrosion Tests in 20% HCl on Some Dilute Alloys Based on Lot A

| Alloying addition -ppm | ppm Cu | ppm Fe | Penetration Time - Days | Percent Weight Loss Per Day |
|---|---|---|---|---|
| None* | 21 | 10 | 3.9, 4.0, 5.1 | 0.56, 0.52, -- |
| 1000 Mn | 20 | 40 | 7 | 0.63 |
| 100 Ca | 25 | 10 | 5½ | 0.68 |
| 1000 Si | 30 | 20 | 4.3 | 0.74 |
| 200 Mg | 40 | 15 | 3.0 | 0.80 |
| 1000 Mg | 35 | 20 | 3½ | 0.79 |

*Lot A contained (in ppm) <1 Mn, <2 Ca, 30 Si, 5 Mg.

## Table III

### Effect of Some Cations (added as chloride) on the Corrosion of Lot A in 16% HCl
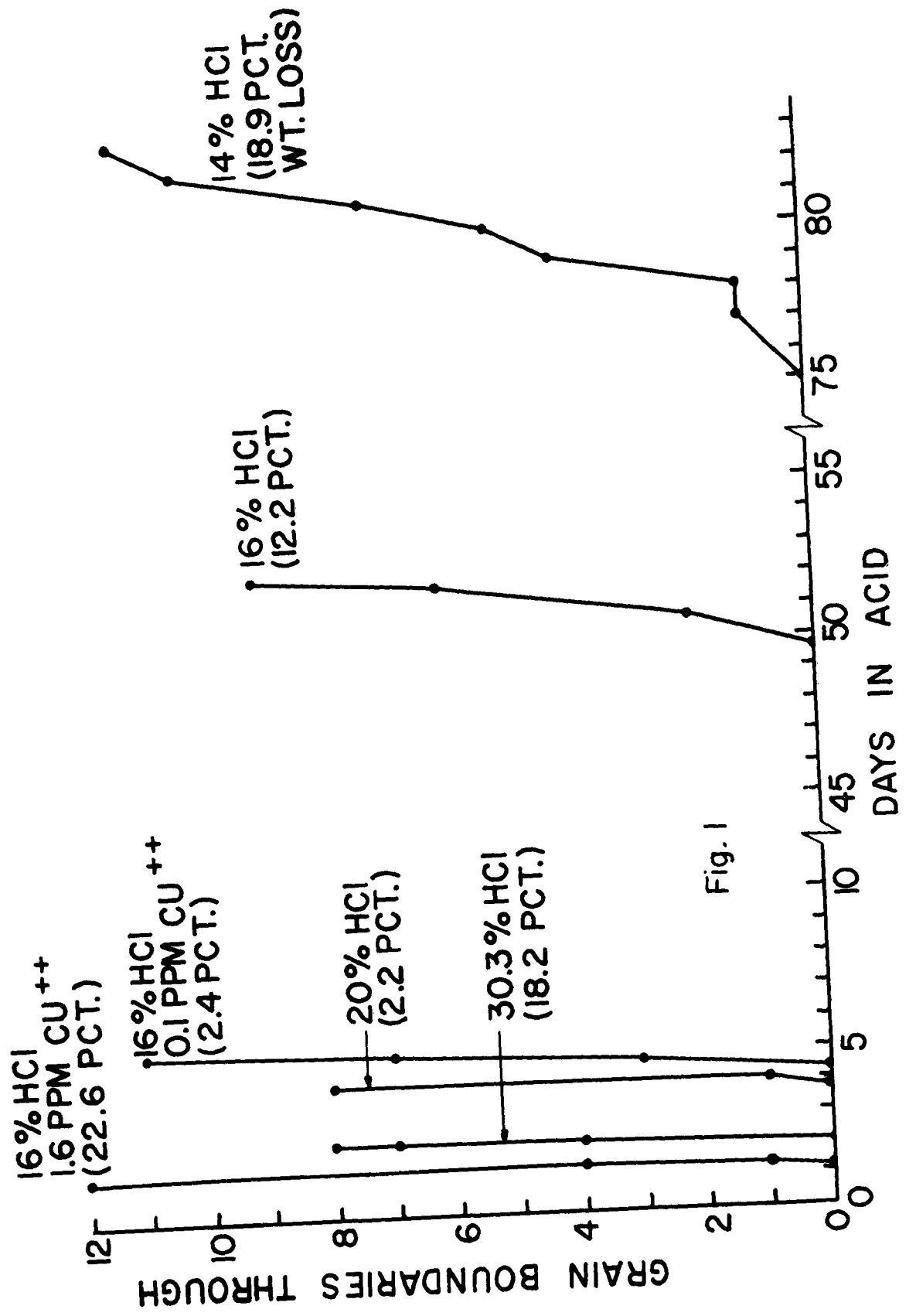
| Addition ppm + | Penetration Time - Days | Pct. Wt. Loss Per Day | $\bar{R}_B/\bar{R}_S$ |
|---|---|---|---|
| None | 32.0, 32.5, 39, 46, 50.1* | 0.23, 0.22, -, 0.22, 0.23* | 14 |
| 0.8 Cu++ | 1.9, 2.0, 3.2 | 13.4, 3.3, 7.4 | 7 |
| 0.8 Ag+ | 2.4 | 6.0 | 9 |
| 0.8 Ni++ | 3.8 | 1.0 | 31 |
| 0.8 Cd++ | 49.1 | 0.25 | 10 |
| 0.8 Pb++ | 57.1 | 0.21 | 10 |
| 100 Pb++ | 6.8 | 0.28 | 65 |

+ Here 0.8 ppm = 0.17 mg

* This test was run at the same time as the others in the Table and is the most suitable for comparison with them.

## Captions for Figs. 1-9

Fig. 1   Number of Grain Boundaries Corroded Through versus Time together with Final Weight Loss for Aluminum A in Hydrochloric Acid of Several Strengths and Cupric Ion Contents.

Fig. 2   Appearance of Specimens of Aluminum A at the End of the Test. One or more of the boundaries in each field has been corroded through except for (e) where this occurred in another field. 26X Diffuse illumination except for (c).
    (a) 16% HCl, 58 days, 13.0% weight loss.
    (b) 18% HCl, 8.1 days, 4.1% weight loss.
    (c) Specimen of (b) illuminated from the rear showing the boundaries corroded through.
    (d) 30.3% HCl, 1.5 days, 18.2% weight loss.
    (e) 37.1% HCl, 6.3 days, 90.2% weight loss.

Fig. 3   Average Rates of Boundary and Surface Penetration for Aluminum A as Functions of Acid Strength. Two to five tests per point. Starred circles represent results of two check tests in which the acid strength was adjusted by preferential evaporation of HCl from the reagent. Hydrochloric acid activity (based on molality) was calculated from the activity coefficients of Akerlöf and Teare.[17]

Fig. 4   Average Rates of Boundary and Surface Penetration for Aluminum A in 16% HCl with Additions of Cupric Ion (as chloride). One to three tests per point. 1 ppm = 0.22 mg.

Fig. 5   General Corrosion in 20% HCl of Seven Aluminums as Functions of Time. Hydrogen evolution curves for K, A, B, C from Reference 14. Points converted from beaker test weight loss data. 100 ml is equivalent to 5% weight loss.

Fig. 6   Penetration Times of Seven Aluminums as Functions of Acid Strength. Lots coded as in Fig. 5.

Fig. 7   Specimen of Aluminum C Which was Undergoing Catastrophic General Corrosion and had Suffered 65.5% Weight Loss after 8.1 Hours in 20% HCl Showing that Intergranular Attack Remains in Advance of Surface Attack. The surface is covered with a black layer of cemented copper. Diffuse illumination. 26X.

Fig. 8   Specimen of Aluminum C after 7.0 Days in 7% HCl.2.5% weight loss. The autocatalytic reaction has produced some small pits within the grains and many pits of the same size or larger at the intergranular grooves so that they appear as ragged bands instead of sharply defined ones (cf. Fig. 2 a and b). Diffuse illumination. 54X.

Fig. 9   Penetration versus Time for Boundary and Surface of Aluminum A in (a) 16% HCl (b) 20% HCl. Boundary data from stepped specimens, surface data converted from measurements of hydrogen evolution[14] (curves) and weight loss (points).

Fig. 1

GRAIN BOUNDARIES THROUGH

DAYS IN ACID

16% HCl
1.6 PPM CU⁺⁺
(22.6 PCT.)

16% HCl
0.1 PPM CU⁺⁺
(2.4 PCT.)

20% HCl
(2.2 PCT.)

30.3% HCl
(18.2 PCT.)

16% HCl
(12.2 PCT.)
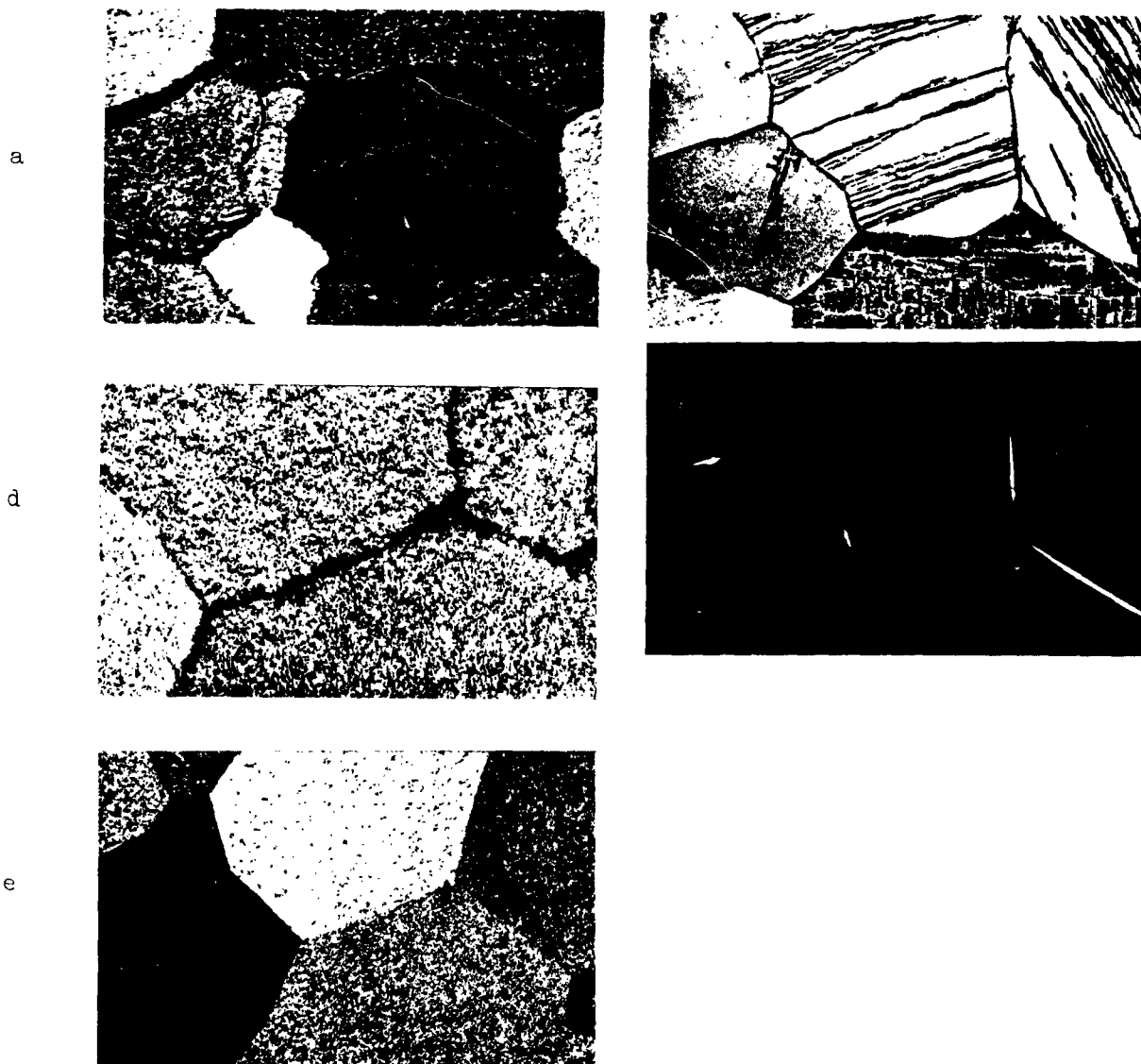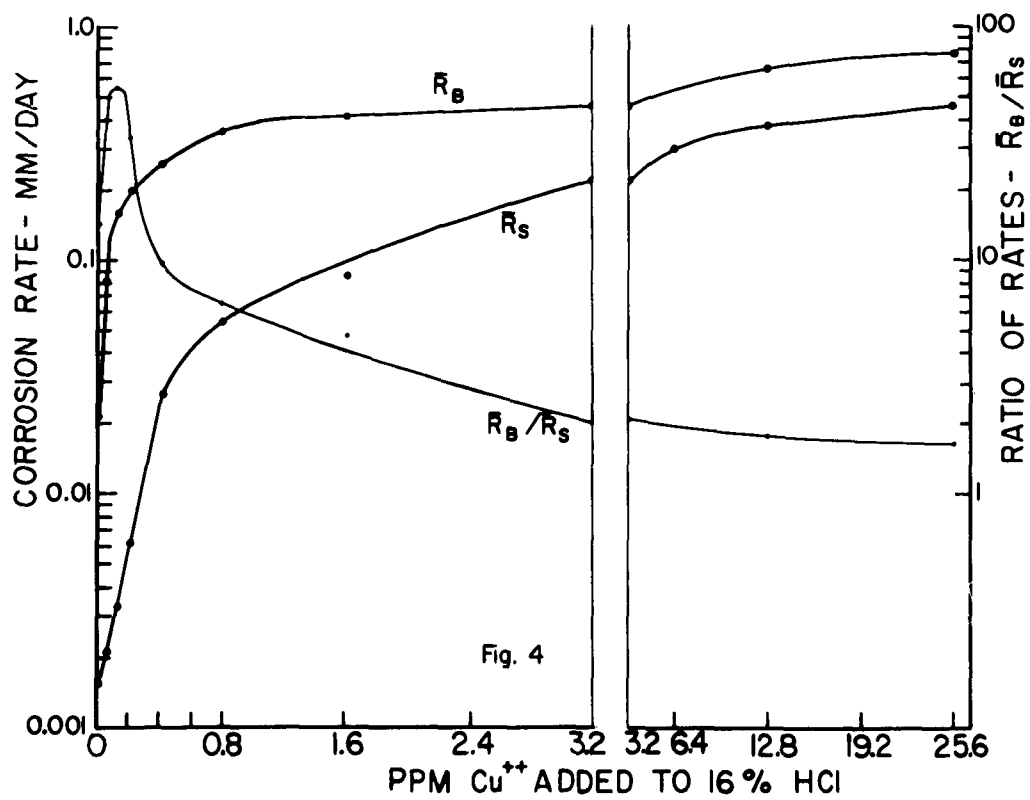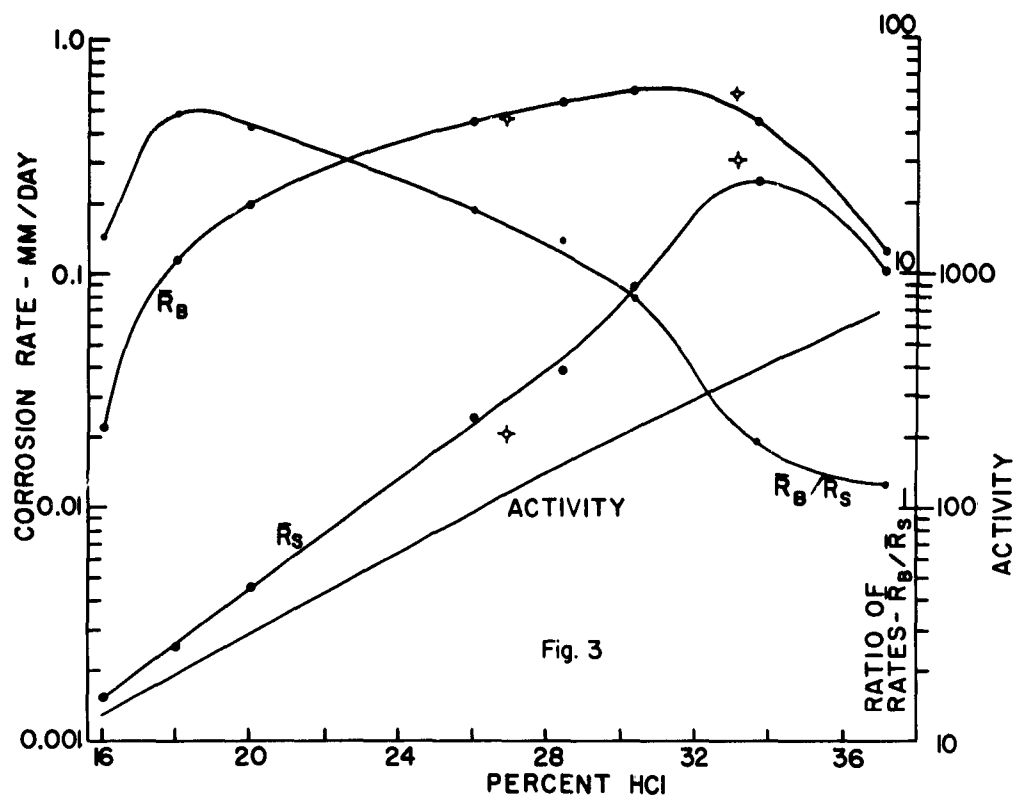
14% HCl
(18.9 PCT.
WT. LOSS)

Fig. 2  Appearance of Specimens of Aluminum A at the End of the Test.  One
or more of the boundaries in each field has been corroded through
except for (c) where this occurred in another field.  Diffuse
illumination except for (c).  26X, reduced by 25%.
    (a) 40% HCl, 58 days, 13.0% weight loss.
    (b) 19% HCl, 8.1 days, 4.1% weight loss.
    (c) Specimen of (b) illuminated from the rear showing
        boundaries corroded through.
    (d) 30.3% HCl, 1.5 days, 18.2% weight loss.
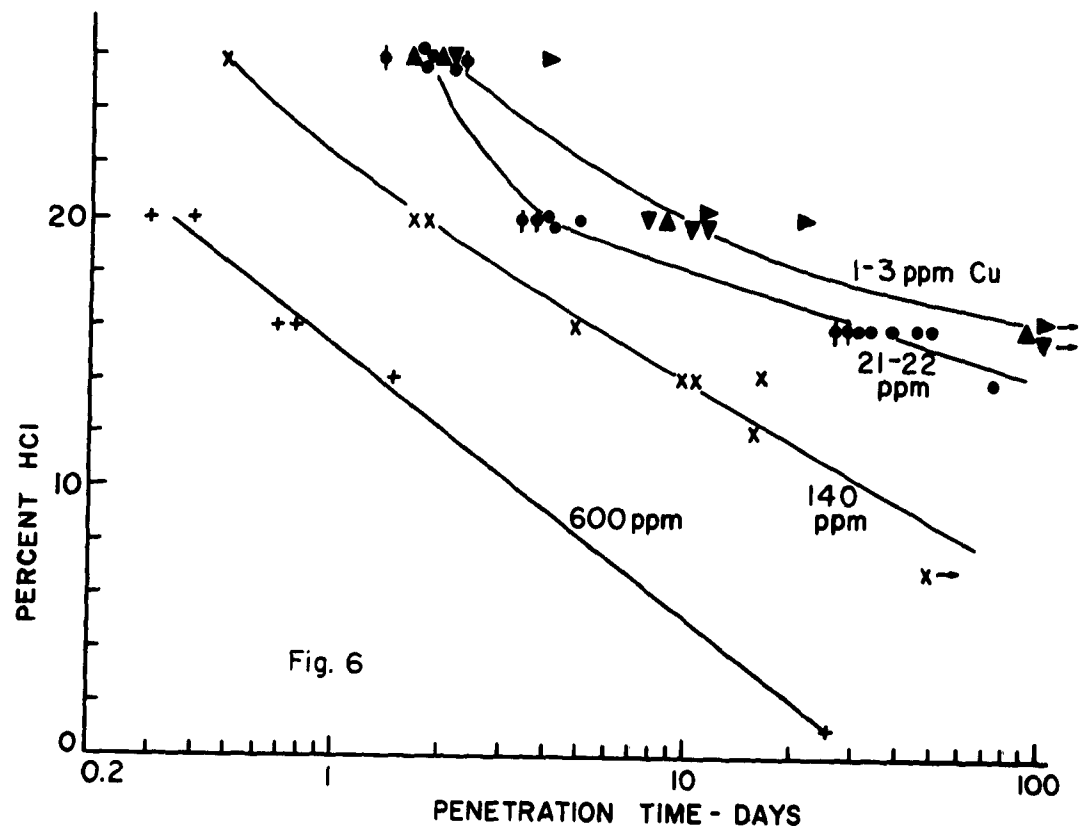    (e) 37.4% HCl, 6.3 days, 90.2% weight loss.

Fig. 3



Fig. 4

Fig. 5

| CODE | ALLOY | PPM Cu |
|------|-------|--------|
| ▶ | H | |
| ▼ | K | 1 |
| ▲ | L | 3 |
| ● | A | 21 |
| ● | P | 22 |
| X | B | 140 |
| + | C | 600 |

MILLILITERS H₂ NTP

HOURS IN 20% HCl

600 PPM

140 PPM

21 PPM

1 PPM CU



Fig. 6

PERCENT HCl

PENETRATION TIME - DAYS

1-3 ppm Cu
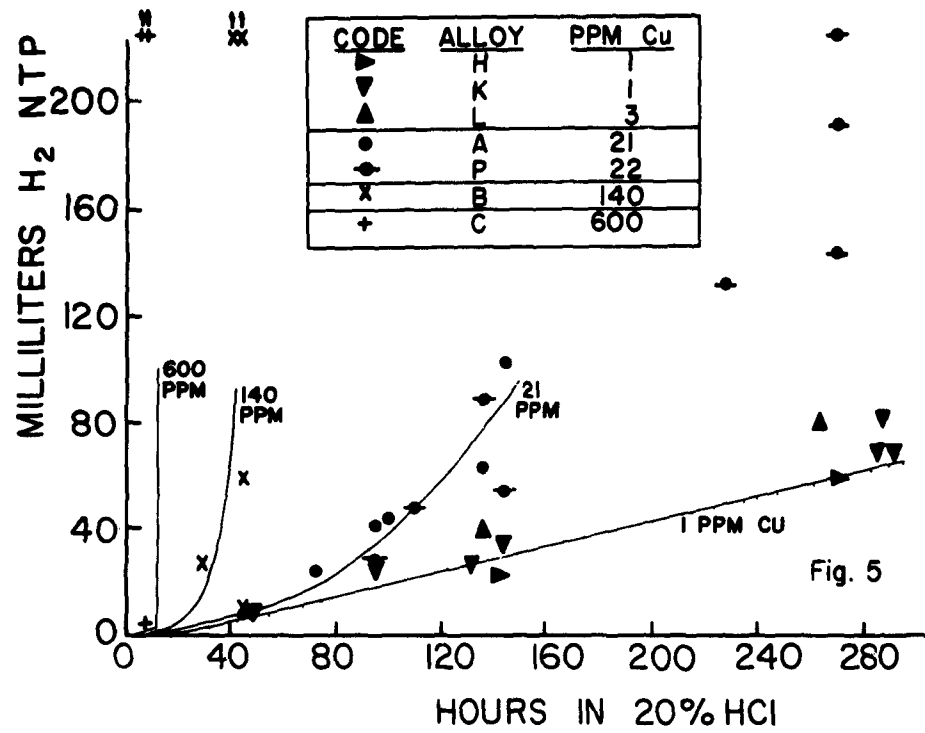
21-22 ppm

140 ppm

600 ppm

Fig. 7   Specimen of Aluminum C Which was Undergoing Catastrophic General
         Corrosion and had Suffered 65.5% Weight Loss after 8.1 hours in
         20% HCl Showing that Intergranular Attack Remains in Advance of
         Surface Attack.  The surface is covered with a black layer of
         cemented copper.  Diffuse illumination. 26X, reduced by 25%.
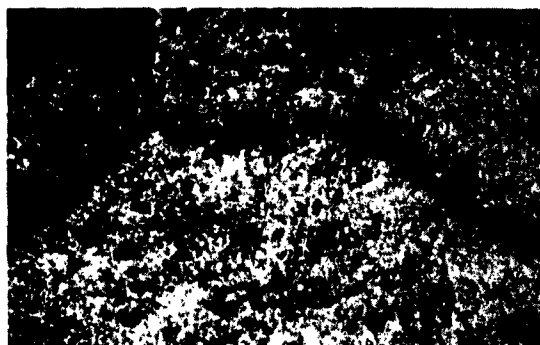


Fig. 8   Specimen of Aluminum C after 7.0 Days in 7% HCl.   2.5% weight
         loss.  The autocatalytic reaction has produced a number of small
         pits within the grains and many pits of the same size or larger
         at the intergranular grooves so that they appear as ragged bands
         instead of sharply defined ones (cf. Fig. 2 a and b).  Diffuse
         illumination.  54X, reduced by 25%.

Fig. 9a



Fig. 9b